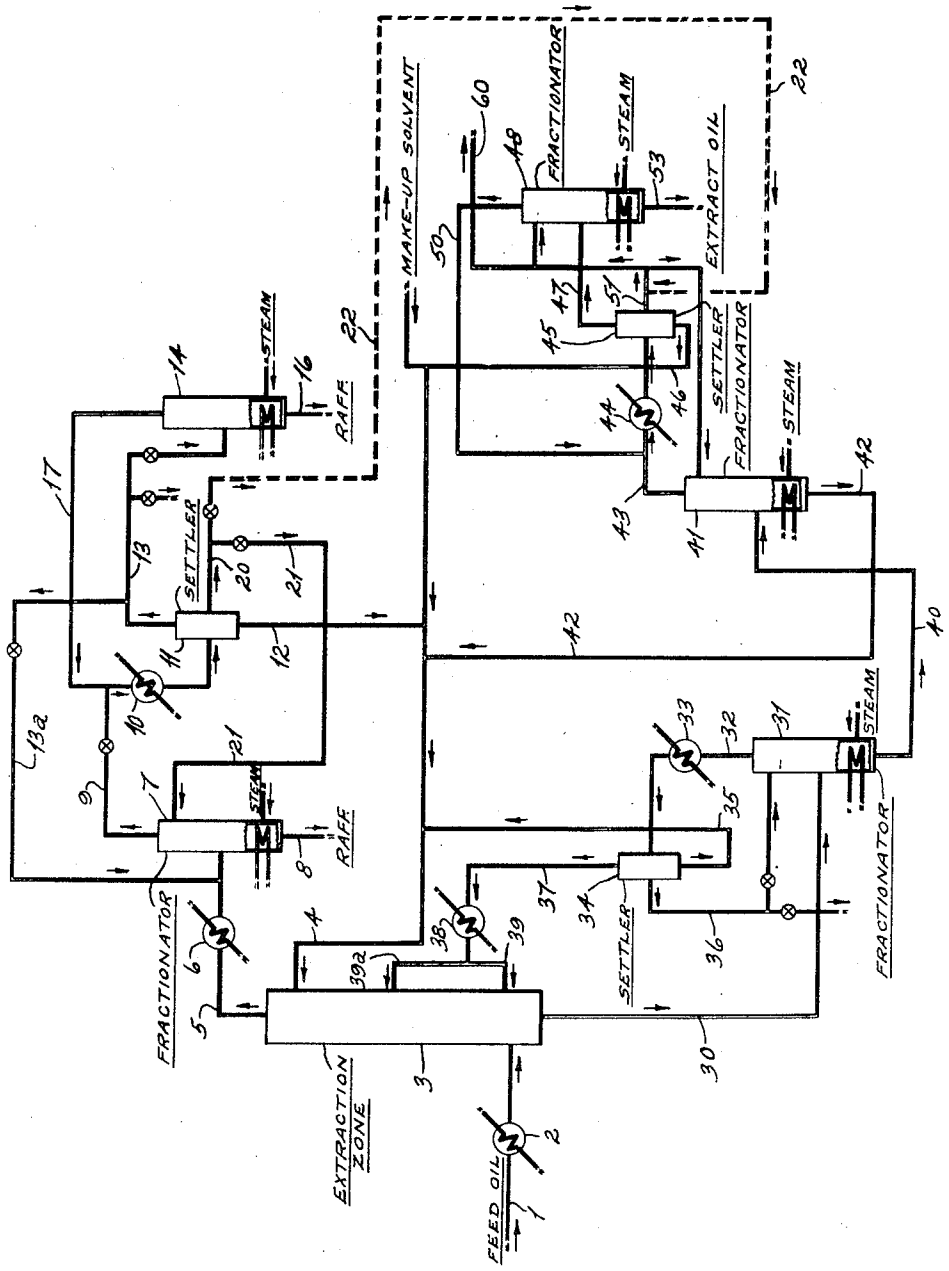
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METHOD OF REFINING OIL WITH A SOLVENT

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METHOD OF REFINING OIL WITH A SOLVENT

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1

This invention relates to a method of refining oil with a solvent liquid which is at least partially miscible with water at ordinary temperatures and particularly relates to the extraction of oil containing constituents whose true boiling point is lower than or in the same boiling range as that of the solvent.

In accordance with the invention, a relatively low boiling feed oil, such as kerosene, is extracted with a selective solvent, such as furfural, in the presence of a small amount of water and under conditions effective to form extract and raffinate phases respectively. The raffinate phase comprises non-aromatic or relatively insoluble constituents of the oil mixed with a small proportion of the solvent and water. The extract phase comprises the relatively aromatic and naphthenic constituents of the oil dissolved in the main body of aqueous solvent.

The extract and raffinate phases are advantageously separately subjected to distillation so as to effect separation of solvent from oil. It is contemplated supplying sufficient steam or water to the fractionating zone in which the raffinate phase is distilled to form a ternary water-oil-solvent azeotrope with all of the solvent present in the raffinate phase mixture. The resulting distillate is condensed and subjected to settling to form oil-rich, water-rich and solvent-rich liquid layers respectively. The oil-rich liquid is removed and treated to recover a small amount of residual solvent retained therein or may be recycled to the distillation zone. The solvent-rich liquid is recycled to the extraction zone. The water-rich liquid is used in part as reflux liquid in the raffinate phase fractionating zone, and the remainder treated to recover the small amount of solvent retained therein.

The extract phase obtained from the extraction zone is distilled in a separate fractionator to which sufficient steam or water is added to form a ternary solvent-water-oil azeotrope with a portion, advantageously the more paraffinic portion, of the extract oil present in the extract phase mixture. The resulting azeotropic distillate is removed, leaving a residual liquid of solvent containing a large or major portion of the extract oil.

The resulting azeotropic distillate is condensed and subjected to settling so as to form oil-rich, water-rich and solvent-rich liquid layers. The oil-rich liquid is recycled to the extraction zone advantageously at a plurality of intermediate points. The solvent-rich liquid is also recycled to the extraction zone advantageously to the upper portion thereof or with fresh solvent

2

while the water-rich liquid is recycled to the extract phase fractionating zone.

The residual liquid comprising the main body of solvent, and extract oil is conducted from the extract phase fractionating zone to a secondary fractionating zone wherein the remaining extract oil is azeotropically distilled from the solvent and treated in a manner substantially similar to that disclosed in our co-pending application Serial No. 777,071, filed September 30, 1947, and which will be described in more detail later.

The invention thus involves recovering solvent as a distillate from the raffinate oil phase and as an oil-free or substantially oil-free liquid residue from the extract phase.

The invention is particularly applicable to the solvent treatment of low boiling oils such as kerosene or fractions of petroleum boiling in the range of about 300 to 650° F. ASTM and comprising constituents which form relatively low boiling azeotropes with the solvent and water. A feature of the invention is that only a small proportion of the total solvent flowing through the process is vaporized in the recovery of the solvent from the oil. As a result, the solvent is subjected to less severe temperatures and therefore subject to less decomposition. Furthermore, where the true boiling point range of the oil includes the boiling point of the solvent, simple fractionation is ineffective to separate the oil and solvent.

A distinguishing feature of the present invention over that disclosed in the previously mentioned co-pending application is that the solvent is recovered from the extract phase mixture in a two-stage ternary azeotrope system, and that the oil recovered in the first ternary azeotrope is recycled to the extraction zone as extract recycle. Recycling of this particular oil to the extraction zone facilitates obtaining a higher yield of high quality raffinate oil and a higher quality extract.

In order to illustrate the invention in more detail, reference will now be made to the accompanying drawing comprising a flow diagram of the process as applied to the treatment of kerosene. The feed oil has an API gravity of about 40.4 and has an ASTM boiling range as follows:

	°F.
I. B. P.	332
10%	365
20%	377
50%	414
90%	482
E. P.	520

As indicated in the drawing, the feed oil is conducted from a source not shown through a pipe 1 and heat exchanger 2 to the lower portion of an extraction tower 3 of conventional type.

The feed oil rises through the packing of the tower countercurrently to a stream of solvent liquid introduced to the upper portion of the tower through a pipe 4. The solvent comprises furfural and minor amounts of water and oil as a result of previous use in the process. It thus contains about 15.0% oil and 3.0% water by volume. It is introduced to the tower in the proportion of about 1 volume of solvent to 2 volumes of feed oil. The temperatures of the entering streams of oil and solvent are regulated, so that the temperature at the bottom of the tower is maintained at about 100° F., while the temperature at the top is maintained at about 150° F.

Under these conditions, extract and raffinate phases are formed. The raffinate phase comprises oil amounting to from about 60 to 80% by volume of the feed oil. The raffinate phase is continuously removed from the upper portion of the tower 3 through a pipe 5 and heat exchanger 6 to a fractionator 7. Heat may be supplied to the bottom of the fractionator either with open steam, a closed heating coil, or a combination of both. As will be mentioned later, provision is made for supplying reflux liquid to the top of the tower. Sufficient water is introduced to the tower either in the form of steam or water reflux or both to form the ternary water-oil-furfural azeotrope with all of the furfural present in the raffinate phase feed. The top of this tower is maintained at a temperature of about 205 to 250° F., and the bottom at a temperature of about 250 to 400° F., so that the solvent is completely or substantially completely distilled from the raffinate oil, the solvent-free oil being discharged through a pipe 8.

The distillate comprising solvent, water, and a small amount of oil is removed through pipe 9 into condenser 10 to a settling chamber 11. The settler is maintained at a temperature of about 70 to 150° F., and the condensate separates into oil-rich, water-rich, and solvent-rich liquid layers respectively. These layers have the following approximate composition:

	Furfural	Oil	Water
	Per cent	*Per cent*	*Per cent*
Oil-rich layer	4–6	94–96	0.1–0.2
Water-rich layer	6–7	0.1	94–93
Furfural-rich layer	80–82	15	3

The solvent-rich liquid is continuously drawn off through pipe 12 which communicates with pipe 4 by which this liquid is recycled to the extraction tower 3.

The oil-rich liquid is drawn off from the top of the settling chamber through a pipe 13. If not recycled to tower 7, it is passed to a secondary fractionator 14 wherein it is subjected to azeotropic distillation, sufficient water being injected into the fractionator either in the form of open steam or water reflux to form the ternary azeotrope of furfural, oil, and water, the operation of this fractionator being conducted so as to effect recovery of raffinate oil from the oil-rich liquid. The recovered oil is discharged through pipe 16, while the distillate from this fractionator is recycled through a pipe 17 to the settling chamber 11. The oil discharged through pipe 16 has the following approximate characteristics:

API gravity	46.0
ASTM distillation:	
I. B. P.	271
10%	315
20%	327
50%	374
90%	445
E. P.	502

The water-rich liquid is drawn off through pipe 20, and at least a portion thereof diverted through pipe 21 for recycling to the top of the fractionator 7 as reflux liquid. The non-recycled portion of this liquid can be separately treated to recover residual furfural and any oil therefrom. On the other hand, and as will be described later, it may be conducted through pipe 22 for treatment with water-rich liquid recovered from the treatment of the extract phase to which reference will be made later.

The extract phase collecting in the bottom of the extraction tower 3 is continuously drawn off through pipe 30 to a primary extract phase fractionator 31. This fractionator is also provided with means for supplying heat to the bottom thereof, either in the form of open steam or a closed heating coil or both, provision being made also for the introduction of reflux liquid. Sufficient water is injected into the fractionator to form a ternary furfural-oil-water azeotrope with a minor portion of the extract oil. This azeotrope is thus removed as a distillate through pipe 32 and a condenser 33 from which it is passed to a settling chamber 34 wherein it separates into oil-rich, water-rich and solvent-rich liquid layers respectively.

The solvent-rich liquid is drawn off through pipe 35 which communicates with pipe 4 for return to the extraction zone. The water-rich liquid is drawn off through pipe 36 and recycled as reflux to the fractionator 31.

The oil-rich liquid is drawn off through pipe 37 and heat exchanger 38 from which it is discharged through a plurality of branch pipes 39 and 39—A for introduction at one or more intermediate points of the extraction tower.

The amount of oil injected through pipes 39 and 39—A will depend upon the nature of the feed oil, the extraction temperature, and the degree of solvent fractionation desired. Usually, it will amount to about 1.0 to 10.0% by volume of the feed oil. The injected oil is the relatively paraffinic portion of the extract and will have the following approximate characteristics:

API gravity	47.1
ASTM distillation:	
I.B.P.	268
10%	310
20%	330
50%	375
90%	443
E. P.	512

Operation of the fractionator 31 is regulated so as to produce the desired quantity of oil for this extract recycle.

The residual liquid drawn off from the bottom of the fractionator 31 comprises the main body of furfural used in the extraction zone containing the major portion of the extract oil. It is conducted through pipe 40 to a secondary extract phase fractionator 41 substantially similar to the fractionator 31. Sufficient water in the

form of steam or reflux is injected through fractionator 31 to form the ternary oil-furfural-water azeotrope with substantially all of the extract oil present in the feed stream flowing through pipe 40. The temperature at the top of the fractionator will be about 205 to 250° F. and that at the bottom will be about 250 to 400° F. The amount of water required for forming the azeotrope is about 5 to 50% by volume of the feed mixture flowing through pipe 40.

Substantially oil-free solvent is drawn off from the bottom of fractionator 41 through pipe 42 which communicates with pipe 4.

The resulting distillate containing extract oil is conducted through pipe 43 and condenser 44 to a settling chamber 45 maintained at about 70 to 150° F. Separation into oil-rich, water-rich and solvent-rich liquid layers occurs. The solvent-rich liquid is drawn off through pipe 46 and conducted through pipe 4.

The oil-rich liquid is drawn off through pipe 47 and introduced to a tertiary fractionator 48 substantially similar to the preceding fractionator. In this fractionator, the residual solvent retained in the oil-rich liquid is distilled therefrom as an azeotrope. The resulting distillate is advantageously recycled through pipe 50 to the settling chamber 45.

The water-rich liquid from chamber 45 is drawn off through pipe 51 and, in part, used as reflux in fractionator 48, and, in part, as reflux in fractionator 41.

The solvent-free extract oil is discharged from fractionator 48 through pipe 53.

The extract oil discharged through pipe 53 is of the following character:

A. P. I. gravity		37.1
ATSM distillation:		
I. B. P.	°F.	345
10%	°F.	368
20%	°F.	382
50%	°F.	420
90%	°F.	495
E. P.	°F.	530

As previously mentioned, some of the water-rich liquid obtained in the settler 11 can be drawn off through pipe 22 and added to the liquid flowing through pipe 51.

In the event that there is surplus water-rich liquid from the settler 34 beyond that required for refluxing the fractionator 31, this surplus liquid can also be passed to fractionator 48.

In order to avoid a build-up of water in the system, provision may be made for diverting a portion of the water-rich liquid from settler 45 through pipes 51 and 60, and subjecting the diverted stream to stripping in a separate fractionator so as to strip the small amount of retained solvent from the excess water which latter can then be dicharged.

While the treatment of kerosene has been specifically referred to in connection with the drawing, nevertheless, it should be understood that the process is applicable to the treatment of other types of oils and also to the treatment of gas oil containing, usually in small amounts, constituents having a true boiling point lower than or in the same boiling range as that of the solvent used. In general, it has application to the treatment of hydrocarbon mixtures having an ASTM boiling range of about 275 to 600° F. It is also contemplated that it has application to the treatment of oils derived from animal and vegetable sources. Specific conditions of temperature and solvent dosage may vary from those specifically mentioned, depending on the character of the feed oil undergoing treatment and the degree of fractional separation desired in the extraction tower 3.

The invention is particularly concerned with the use of relatively high boiling organic solvent liquids which are miscible, at least to some extent with water, and with which constituents of the oil feed in the presence of water form azeotropes. Selective solvents other than furfural may be used. They may include other derivatives of the furan group and other aldehydes such as benzaldehyde nitrobenzene and ketones, etc.

Obviously many modifications and variations of the invention as above set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. In the solvent refining of feed oil of the class consisting of kerosene and gas oil containing at least a small proportion of naturally occurring constituents having true boiling points in the range of the solvent boiling temperature and below wherein the feed oil is subjected to contact in an extraction tower in the presence of water with a water miscible organic solvent liquid having selective solvent action as between paraffinic and non-paraffinic constituents of the oil, extract and raffinate phases respectively lean and rich in paraffinic constituents of the oil are formed, said phases separately removed from the extraction zone, each of said removed phases comprising oil, solvent and water, and the removed phases treated to recover solvent from the oil for reuse in the extraction zone, the method comprising recovering solvent from the removed raffinate phase, recycling so-recovered solvent to the extraction zone, separately distilling from said extract phase in the presence of added water in a primary fractionating zone, a distillate containing ternary azeotrope of solvent, oil and water, the oil in said azeotrope being the relatively paraffinic portion of the extract oil and amounting to a relatively minor proportion of the extract oil, and forming a residual liquid fraction comprising the main body of solvent liquid contained in the extract phase removed from the extraction zone and in addition the remainder and major portion of the extract oil, substantially completely condensing said primary distillate, subjecting resulting condensate to settling in a primary settling zone thereby forming oil-rich, water-rich and solvent-rich liquid layers respectively, said oil-rich layer comprising substantially all of said azeotrope oil, recycling said oil-rich layer to the extract phase zone of the extraction tower, recycling said solvent-rich layer to the raffinate zone of said extraction tower, recycling at least a portion of the water-rich layer as reflux to the primary fractionating zone, passing said residual liquid fraction to a second fractionating zone, subjecting it therein to distillation in the presence of water to form a second distillate of ternary azeotrope containing substantially all of the remaining extract oil, and a second residual liquid fraction comprising substantially oil-free solvent, said oil-free solvent being the bulk of the solvent removed from the extraction zone in the extract phase, returning said oil-free solvent fraction to the extraction zone, con-

densing said secondary distillate and separately recovering extract oil and residual solvent therefrom.

2. The method according to claim 1 in which the solvent liquid is furfural.

3. The method according to claim 1 in which the paraffinic oil contained in the first-mentioned ternary azeotrope amounts to about 1 to 10% by volume of the feed oil passing to the extraction zone.

4. The method according to claim 1 in which the solvent comprises furfural and in which the relatively paraffinic oil contained in the said first-mentioned azeotrope amounts to about 1 to 10% by volume of the feed oil passing to the extraction zone.

5. In the solvent refining of feed oil of the class consisting of kerosene and gas oil containing at least a small proportion of naturally occurring constituents having true boiling points in the range of the solvent boiling temperature and below wherein the feed oil is subjected to contact in an extraction tower in the presence of water with a water miscible organic solvent liquid having selective solvent action as between paraffinic and non-paraffinic constituents of the oil, extract and raffinate phases are formed, respectively lean and rich in paraffinic constituents of the oil, said phases separately removed from the extraction zone, each of said removed phases comprising oil, solvent and water, and the removed phases treated to recover solvent from the oil for re-use in the extraction zone, the method comprising recovering solvent from the removed raffinate phase, recycling so recovered solvent to the extraction zone, separately distilling from said extract phase in the presence of added water in a primary fractionating zone, a distillate containing ternary azeotrope of solvent, oil and water, the oil in said azeotrope being the relatively paraffinic portion of the extract oil and amounting to a relatively minor proportion of the extract oil, and forming a residual liquid fraction comprising the main body of solvent liquid contained in the extract phase removed from the extraction zone and in addition the remainder and major portion of the extract oil, substantially completely condensing said primary distillate, subjecting resulting condensate to settling in a primary settling zone thereby forming oil-rich, water-rich and solvent-rich liquid layers respectively, said oil-rich layer comprising substantially all

of said azeotrope oil, recycling said oil layer to the extract phase zone of the extraction tower, recycling said solvent-rich layer to the raffinate zone of said extraction tower, recycling at least a portion of the water-rich layer as reflux to the primary fractionating zone, passing said residual liquid fraction to a second fractionating zone, subjecting it therein to distillation in the presence of water to form a second distillate of ternary azeotrope containing substantially all of the remaining extract oil, and a second residual liquid fraction comprising substantially oil-free solvent, said oil-free solvent being the bulk of the solvent removed from the extraction zone in the extract phase, returning said oil-free solvent fraction to the extraction zone, condensing said secondary distillate, subjecting resulting secondary condensate to settling in a secondary settling zone, forming in said secondary settling zone secondary oil-rich, solvent-rich and water-rich liquid liquid layers respectively, recycling secondary water-rich liquid in part as reflux to said secondary fractionating zone, stripping residual solvent from the remainder of said secondary water-rich liquid, recycling secondary solvent-rich liquid to the extraction tower, passing the secondary oil-rich liquid to a tertiary fractionating zone, distilling therefrom a tertiary distillate containing solvent and leaving a substantially solvent-free extract oil as residual liquid, discharging said solvent-free extract oil and recycling said tertiary distillate to said secondary settling zone.

6. The method according to claim 5 in which the solvent liquid comprises furfural.

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